

somewhat toward the red.⁴ At low concentrations it would not be detected and it is probably photolyzed under the conditions of our experiments (and those of Frey and Stevens²) to yield ethylene.

This work was undertaken in part to discover whether photoisomerization (reaction 2) did occur and whether we could study wave length and pressure effects on the reaction. Thus far we have observed very little effect of added nitrogen on the yield of diazomethane. The lack of an effect may be due to concomitant destruction of diazomethane by the stray light from the monochromator. Thus far, then, we are unable to make any statement regarding the relative importance of reactions 3 and 4 in producing methylene. One may make arguments for either reaction 3 or 4, or a combination of the two, being primarily responsible for the average properties of methylene formed in the photolysis.² Frey and Stevens did not take the photoisomerization and consequent diazomethane photolysis into account in determining the average properties of the methylene from diazirine,² so the results of their experiments probably should be reassessed.

It is also possible that diazo compounds are intermediates in the pyrolysis of diazirines. Frey and Stevens⁵ point out this possibility and the close correspondence of the activation energy for dimethyldiazirine decomposition, 33 kcal./mole, with the activation energy for diazomethane decomposition, 35 kcal./mole.⁶ In the light of our results it seems that the intermediacy of diazo compounds in the chemistry of the diazirines must be considered.

We are improving our experimental set-up to allow irradiation with more nearly monochromatic light and will report more detailed pressure and wave-length dependencies for this system in the near future.

Acknowledgments.—We are grateful to Dr. William Graham for the gift of a sample of diazirine. We thank the National Science Foundation and the Research Corporation for grants and M. J. A. also thanks the NSF-URPP for support.

(4) H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 3514 (1963).

(5) H. M. Frey and I. D. R. Stevens, *ibid.*, 3865 (1962).

(6) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

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Intramolecular Ligand Exchange in Seven-Coordinate Structures

Sir:

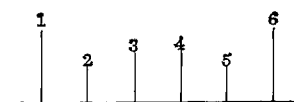
We find that the F^{19} n.m.r. spectrum of highly purified IF_7 consists of a broad, symmetrical two-line pattern with a peak separation of about 4400 c.p.s. at 56.4 Mc. ($\delta = -254$ p.p.m., CF_3COOH).² The peak separation is field independent and thus the two peaks do not represent chemically shifted nuclei. A careful search failed to reveal any other resonance. The spectrum sharpens slightly with temperature increase, and it is not grossly altered in going from liquid IF_7 to solutions of IF_7 . We conclude that there is spectroscopic equivalence of fluorine atoms in IF_7 by the following reasoning.³ The F^{19} n.m.r. spectrum of seven

(1) Iodine heptafluoride was stored in a stainless steel cylinder over sodium fluoride for six months and then carefully fractionated in a quartz vacuum system fitted with Delmar-Urry "O" ring connectors and compression valves in which the "O" rings and bores were made from fluorocarbon elastomers and resins. Our samples of IF_7 did not attack quartz over a long period of time.

(2) Our observation is in agreement with those of (a) L. G. Alexakos, C. D. Cornwell, and S. B. Pierce, *Proc. Chem. Soc.*, 341 (1963); (b) L. W. Reeves, E. J. Wells, N. Bartlett, and S. Beaton, private communication.

(3) H. S. Gutowsky and C. J. Hoffman reported a "multiple" IF_7 F^{19}

spectroscopically equivalent fluorine atoms bound to a single iodine ($I = 5/2$) atom should be a sextet with a symmetrical variation in line width if the rate of quadrupolar relaxation is slow⁴:



Using Anderson's⁵ theory on exchange and motional narrowing in n.m.r. spectral lines together with the transition probabilities predicted by Pople's theory,⁴ it can be shown that, as the rate of quadrupolar relaxation is increased, lines 1 and 6 and 3 and 4 move toward the center of the pattern while 2 and 5 move outward. The relative rates of shift of the pairs of lines are 2025:216:783 for the lines pairs 1,6:3,4:2,5, respectively. As the lines shift, they also broaden considerably. At intermediate rates of quadrupolar relaxation, the composites of lines 1 through 6 will comprise a symmetrical two-line pattern as is observed. A possible representation is sketched in Fig. 1; this is not a unique

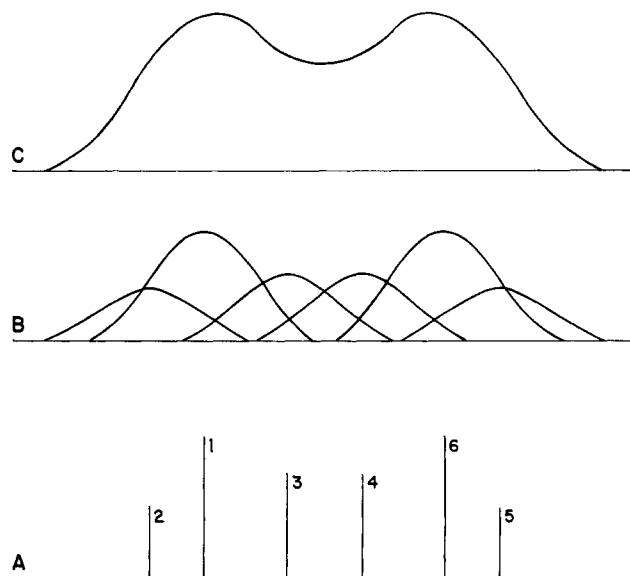


Fig. 1.—Calculated F^{19} n.m.r. spectrum for the case of an intermediate quadrupolar relaxation rate in iodine heptafluoride: A, position of lines; B, estimated line shapes; C, resultant F^{19} spectrum.

solution nor have line shapes been rigorously calculated. Consistent with our interpretation of an intermediate rate of quadrupolar relaxation for liquid IF_7 , the F^{19} spectrum sharpens slightly on temperature increase to $\sim 100^\circ$, broadens significantly for IF_7 solutions at -78° , and as reported by Alexakos, Cornwell, and Pierce^{2a} is a single resonance for gaseous IF_7 . The magnitude of the IF coupling constant is of the order of 1000 c.p.s.

There is spectroscopic (n.m.r.) equivalence of fluorine atoms in ReF_7 ⁶; a single resonance is observed at low field.^{2b} It is presumed that in the rhenium case there is faster quadrupole relaxation than in IF_7 so that any vestige of Re-F coupling is lost. The quadrupole moments of Re^{185} and Re^{187} are about 4.5 times as large as that of I^{127} .

We suggest that the ground states of odd numbered high-coordinate structures commonly have close-lying

spectrum and interpreted this as showing nonequivalent fluorine nuclei [*J. Chem. Phys.*, **19**, 1259 (1951)].

(4) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

(5) P. W. Anderson, *J. Phys. Soc. Japan*, **9**, 316 (1954).

(6) H. Selig and E. L. Muetterties, unpublished work. Data were obtained for liquid ReF_7 and for ReF_7 solutions in WF_6 .

vibronically excited states which provide a mechanism for time-averaging the ligand environments and that this is the origin of fluorine atom equivalence, on the n.m.r. time scale, for IF_7 and ReF_7 . A case for fast, intramolecular ligand exchange was made earlier for five-coordinate structures^{7,8} and will be more thoroughly documented in another paper.⁹

(7) S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(8) E. L. Muettterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(9) E. L. Muettterties, K. J. Packer, W. Mahler, and R. Schmutzler, to be published.

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Biological Interconversions in the Amaryllidaceae. I. The Haemanthamine-Haemanthidine-Tazettine Sequence¹

Sir:

Sprekelia formosissima (L.) contains three principal alkaloids²: haemanthamine (I),³ haemanthidine (II),⁴ and tazettine (III),⁵ whose structures suggest the existence of the biological sequence $\text{I} \rightarrow \text{II} \rightarrow \text{III}$. An early indication of this was based on our observation that highest yields of I are obtained early in the flowering season while III predominates in later collections. Although the yield of II varies, its relationship to tazettine was considered on the basis of its facile conversion to the latter by the action of methyl iodide and dilute base⁶ which must involve a hydride transfer.⁴

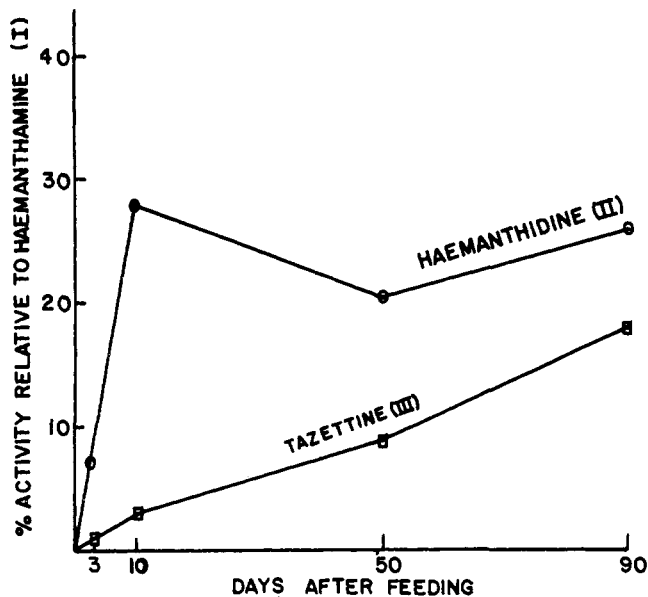


Figure 1.

We have shown now that the above sequence does in fact occur *in vivo*. Tritiated haemanthamine (I)⁷

(1) Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962. The most recent paper on this subject is D. A. Archer, S. W. Breuer, R. Binks, A. R. Battersby, and W. C. Wildman, *Proc. Chem. Soc.*, 168 (1963).

(2) H.-G. Boit and H. Ehmke, *Chem. Ber.*, **88**, 1590 (1955).

(3) H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, **82**, 197 (1960).

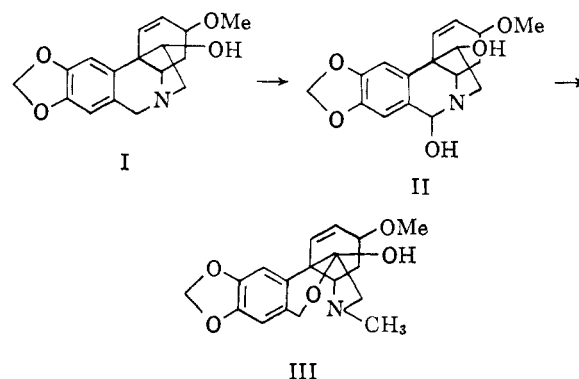
(4) S. Uyeo, H. M. Fales, R. J. Highet, and W. C. Wildman, *ibid.*, **80**, 2590 (1958).

(5) T. Ikeda, W. I. Taylor, Y. Tsuda, S. Uyeo, and H. Yajima, *J. Chem. Soc.*, **80**, 4749 (1956).

(6) W. C. Wildman, *Chem. Ind. (London)*, 1090 (1956).

(7) Tritiation was conducted by combining 50 mg. of I with 0.2 ml. of

was administered to flowering *Sprekelia formosissima* by injection into the flower stems at pH 5.3–5.8. Samples were collected over 90 days, extracted, and the alkaloids were purified by thin-layer chromatography⁸ and crystallization, affording the specific activities of II and III relative to I as a function of time indicated in Fig. 1. The rates of incorporation clearly support the sequence postulated, $\text{I} \rightarrow \text{II} \rightarrow \text{III}$.



In a confirmatory experiment radioactive I, II, and III were readministered to *S. formosissima*. The results (Table I) indicate that the conversion of I to II as well as II to III are essentially irreversible, although a small amount of III may have been recycled to I.⁹

TABLE I

Alkaloid fed (d.p.m./mmole)	% dilution and conversion ^a			Activity of N-methyl- hydrastimide relative to alkaloid
	I	II	III	
I (16.7×10^6)	28.0	7.24	5.16	1.05
II (120×10^6)	0.00	18.0	6.69	0.97
III (352×10^6)	(1.14) ^b	0.077	13.1	0.98

^a (D.p.m./mmole alkaloid recovered \div d.p.m./mmole alkaloid fed) $\times 100$. ^b See Ref. 9.

Each of the three isolated alkaloids was oxidized with potassium permanganate, and the hydrastimic acid was converted to its N-methylimide with methylamine. The activity of the imide relative to the corresponding alkaloid is given in the last column of Table I, and illustrates that all of the tritium resides in the aromatic A ring and has not been scrambled during the experiment.

Biological hydroxylation α to an amino nitrogen is well known¹⁰ and $\text{I} \rightarrow \text{II}$ appears straightforward. Whether $\text{II} \rightarrow \text{III}$ proceeds directly through reaction of II with the usual methyl donor, (+)-S-adenosyl-L-methionine,^{11,12} or occurs *via* the methylation of nortazettine (III, no N-methyl)⁴ remains unanswered. However, these experiments do show that the precursor of tazettine is haemanthidine rather than small fragments as originally proposed.¹³

tritiated acetic acid and 35 mg. of palladium-on-charcoal and heating the mixture at 80° overnight (New England Nuclear Corp., Boston, Mass.). Purification and dilution gave material of 16.7×10^6 d.p.m./mmole.

(8) Chloroform-ethyl-acetate-methanol (20:20:10) separated I and II (R_f 0.29) from III (R_f 0.57) on silica gel "G" while chloroform-methanol-diethylamine (92:3:2) separated I (R_f 0.33) from II (R_f 0.13).

(9) The sample of III fed was later analyzed and found to contain 0.88% of its radioactivity in the form of I.

(10) C. Mackenzie, "Amino Acid Metabolism," Johns Hopkins University Press, Baltimore, Md., 1955, p. 684.

(11) For leading references see S. H. Mudd and J. D. Mann, *J. Biol. Chem.*, **238**, 2164 (1963).

(12) O-Methylation requiring (+)-S-adenosyl-L-methionine has been observed in the Amaryllidaceae [H. Fales, J. D. Mann, and S. H. Mudd, *J. Am. Chem. Soc.*, **85**, 2025 (1963)].

(13) D. H. R. Barton and T. Cohen, "Festschrift A. Stoll," Birkhauser, Basle, 1957, p. 127.